The Effect of Oil Extraction on Porosity and Methane Adsorption for Dry and Moisture-Equilibrated Shales

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Abstract

The porosity and methane adsorption capacity of shale used to estimate gas in place (GIP) are affected both by moisture and oil residing in the pore structure. As well as oil naturally present from maturation, this can include contaminant drilling mud fluids used for drilling. To demonstrate the impact of extractable oil on methane adsorption capacity for both dry and moisture-equilibrated shales, two overmature shales from China (SH1, SH2) and two lower mature shales from UK (BS3, GH4) have been investigated. The oils extracted in low yield from the overmature shales (<0.5 wt.% TOC) arise from oil-based drilling mud, while the much higher yields from the lower maturity UK shales (1.1-2.5 wt.% TOC) is mainly oil generated by maturation. After extraction, minimal changes

(<5%) in total nanopore volume (<100 nm) were observed for the dry over mature shales, but significant increases (95 and 176%) were observed for the dry lower maturity shales. More than 60% of the extracted oil resides in micro and mesopores, and removal could unblock the micropore necks and enlarge the accessible meso and macropore volume. Moisture contents are lower for extracted shales, with reductions of 7-37% observed. Methane equilibrium adsorption capacities increased after oil extraction for both the dry and wet shales, especially for lower maturity shales, where increases were over 200% for the wet shales. Henry's Law was used to show that there were not significant amounts of dissolved methane in oils for the dry shales. Extracting oil from shales prior to determining the porosity and methane adsorption capacity can lead to the GIP being over-estimated for moisture equilibrated shales, particularly for oil-window shales where a reduction of 22% was obtained for the shale investigated here.

Key words: Shale; Maturity; Oil extraction; Methane adsorption; Gas in place.

Highlights:

1. Over 60% extractable oil from oil-window shale is stored in the micro-mesopores.
2. Oil extraction has limited impacts on overmature dry shales.
3. Moisture contents of wet shales reduce by 7-37% after oil extraction.
4. Extraction increases micropore and methane adsorption capacities up to 282%.
5. GIP for oil-window shale can be over-estimated up to 22% by extracting the oil.

1. Introduction

The organic matter in shales comprises mainly the insoluble organic matter, kerogen (typically > 90%), with small amounts of extractable bitumen or oil (typically <10%) [1] removed with common organic solvents [2-4]. Thermal maturity is the critical parameter to indicate the evolution stages of shale oil and gas generation [5, 6]. Shale can be categorized as thermally immature, mature, high maturity, and post or over-mature in terms of capability to generate hydrocarbons. Immature shales with vitrinite reflectance (VR) less than 0.5% Ro, may generate biogenic natural gas. Shales with VRs ranging from 0.5 to 1.3% Ro are in the 'oil window'. High mature shales, VR within the range 1.3-2% Ro in the 'gas window' will generate mainly relatively wet gas, while overmature shales (VR>2% Ro) will generate only dry gas [5-7]. Free gas is stored in the available pore volume, adsorbed gas is mainly in micropores with the greatest surface area, and some gas can dissolve in any hydrocarbons and/or water present [8-12]. Pore networks in shale control the storage and migration of hydrocarbons [13, 14]. The accurate determination of adsorbed gas capacity and porosity is essential for estimating the shale gas in place (GIP), where dissolved gas is normally considered being a relatively minor factor [8, 10, 11, 13, 15].

Both initial [9, 16-18] and solvent extracted [14, 19] shales have been used to relate key factors, including temperature, pressure, composition, and moisture impact on the methane adsorption capacity. The difference between initial and extracted dry shales on porosity and methane adsorption capacity has been studied recently [4, 20-24]. Solvent extraction increases specific surface area (SA) [21, 25]. Methane adsorption in shales can potentially be affected by methane dissolving in any oil present [20-24]. Apart from natural oil arising from maturation [3, 23], oil-based drilling muds, in particular, can also impact methane adsorption and gas dissolution [26]. Oil-based drilling muds are widely used as they do not hydrate active clay minerals, and they can affect further analysis unless proper cleaning methods are applied [2, 27]. Previous researchers have reported

66 that the methane adsorption capacities of the dry extracted shales are larger than for the initial
67 shales [20, 21, 23, 25]. As an example, shales were wiped with dry cloths to remove any drilling fluids
68 before extraction [28]. Different extracted solvents (acetone, tetrahydrofuran (THF), carbon
69 disulfide (CS_2), and benzene) have different impacts on extraction yields since they have different
70 molecular dynamics diameter, aromaticity, boiling point, and polarity, which can lead to various
71 effects on porosity and methane adsorption. However, all these studies on the impact of solvent
72 extraction on methane adsorption and pore characteristics of shales were carried out on dry shales.

73 Water exists under reservoir conditions and moisture significantly reduces the methane adsorption
74 for coals and shales [29-32], making researchers focus on moisture equilibrated shales [10, 14, 33-
75 37]. Water reduces gas adsorption by occupying pore volume and blocking the pore necks, and the
76 GIP estimated for moisture-equilibrated shale is considered more accurate [14, 15]. Gas adsorption
77 for wet shales before and after solvent extraction could be different due to the combined influence
78 of moisture and oil on the pore network. However, to date, the combined impact of moisture and
79 residual oil on the porosity and methane adsorption capacities of shales has not been investigated.
80 Furthermore, for dry shales, previous studies have not addressed the influence of extractable oil on
81 GIP estimates.

82 In this study, high-pressure methane adsorption and low-pressure gas sorption were carried out for
83 dry and moisture-equilibrated shale before and after solvent extraction. For the first time, the
84 impacts of solvent extraction on GIP estimations for both dry and moisture-equilibrated shales are
85 revealed. For the shales investigated, the difference between extractable oil that arise from
86 maturation and that introduced as contaminants from oil-based drilling mud is emphasized.

2. Experimental Methods

2.1 Sample Preparation

Two over-mature shales from China were collected from Ordovician-Lower Silurian Wufeng-Longmaxi Formation, south of Sichuan Basin, with the depth of 4119 m for shale 1 (SH1) and 4098 m for shale 2 (SH2). SH1 and SH2 were selected from different drilling wells [15]. Two lower mature shales from the UK were collected from the Carboniferous Bowland basin, Becconsall (BS3) from a depth of 2143 m, and Grange Hill (GH4) from a depth of 3113 m. To minimize the effect of sample heterogeneity for the following experiments, all the prepared core shales were crushed and sized to 2-4 mm. For solvent extraction, aliquots of the 2-4 mm particles were further crushed to < 250 µm for comparison.

The initial and solvent extracted shale samples were both dried and equilibrated at 95% R.H. moisture (wet) for high-pressure and low-pressure gas sorption experiments. The dry shales were prepared in the vacuum oven (<0.5 mbar) at 120 °C for 48 hours before starting any experiments. The wet shales were prepared in a vacuum desiccator containing saturated potassium nitrate (KNO_3) solution (8 g KNO_3/10 mL H_2O), which can provide 95±2% R.H. moisture equilibration conditions at 20 °C [38-40]. A logger was used to monitor the R.H. and the temperature to make sure the shales reach the moisture equilibration after being kept in the desiccator for 48 hours [15]. The moisture contents for the wet samples were calculated from the mass differences.

2.2 Soxhlet Extraction

Soxhlet solvent extraction was carried out on 20 g of shale using both the 2-4 mm and <250 µm fractions to ensure the particle size has almost no impact on the oil yields. Samples were loaded into the pre-cleaned thimble plugged with cotton by extraction solvent. A mixture of 186 ml dichloromethane (DCM) and 14 ml methanol was used. Extraction was carried out for 120 hours at 40 °C. The solvent was removed after extraction using a rotary evaporator at 35 °C under 400 mbar

pressure. The remaining solvent (about 2 ml) was then collected into a pre-weighed vial and dried until no weight change. The extracted organics yield was calculated by the mass of oil and TOC. Duplicate extractions for each shale were carried out to collect the remaining solvent (about 2 ml) without drying, which was prepared for the GC-MS analysis.

2.3 Elemental Analysis and Vitrinite Reflectance

Shales prepared for elemental analysis were ground into powder (<250 µm). 3 g powder initial shale was treated with sufficient hydrochloric acid (HCl), 1 mol/L, to remove the carbonate. The treated samples were washed with distilled water for 6 times until pH 7 is reached. After carefully decanting the water from the samples, samples were dried in the vacuum oven (<0.5 mbar) at 120 °C for 48 hrs. Then 120 mg of shale was used to determine the total organic carbon (TOC) using a Leco CHN628 elemental analyzer. 1.5 g particle (2-4 mm) shale was used to prepare the polished blocks for the VR (% Ro), measuring the maturity of shales. For the UK shales, the measurement of recognizable vitrinite was made by a LEICA DM4500P microscope with motorized 4-fold turret for reflectance, and data were collected via the Hilgers Fossil Man system connected to the microscope. For the two Chinese over mature shales, bitumen reflectance (BR) measurements were conducted on the polished blocks because of the lack of vitrinite in the Wufeng-Longmaxi shales. The VR was calculated from the BR according to the equation VR = (BR + 0.2443)/1.0495 [41].

2.4 Low-pressure gas (N_2, CO_2) sorption

Low-pressure gas sorption experiments were carried out on both initial and extracted dry and wet shales (2-4 mm particles) by a Micromeritics Surface Area and Porosity Analyser (ASAP 2420) to obtain the pore characters of initial and extracted shales. In this study, Brunauer-Emmett-Teller (BET) theory was used to obtain the surface area (SA) from N_2 sorption, where the relative pressure (P/P°, P is the absolute equilibrium pressure and P° is the saturation pressure) is in the range of 0.05 and 0.2 [42, 43]. Non-Local Density Functional Theory (NLDFT) equilibrium model assuming slit pores

was used to calculate the pore volume from 0.33 to 100 nm [12, 44, 45]. Compared with the Barrett-Joyner-Halenda (BJH) model, the NLDFT model can give a more realistic description of micropore filling while using the BJH model is always leading to an underestimation of pore sizes of micropores and even smaller mesopores [43, 46-48]. 4 g dry and wet particle shales was used for the low-pressure N_2 sorption experiments, and 2 g dry shale was prepared for CO_2 adsorption.

The shale samples were degassed under high vacuum (<0.013 mbar) at 120 °C for 15 hours before dry low-pressure (N_2, CO_2) sorption experiments. To ensure the wet samples were not exposed to vacuum at higher temperatures, the wet shale samples were frozen in liquid N_2 first before manually evacuating the sample tube and starting the low-pressure N_2 sorption analysis. The mass deviation of wet samples before and after analysis was ±0.002%. The P/P° of low-pressure N_2 sorption analysis is set from 10^{-7} to 0.995 P/P°, and all the analysis was performed at -196 °C in a liquid N_2 bath. The low-pressure CO_2 sorption analysis was carried out at 0 °C with a P/P° from 6×10^{-5} to 3.5×10^{-2}, with absolute pressure is from 0.002 to 1.2 bar, to characterize the ultra-microporous structure (<0.8 nm) of dry shales [14, 49].

CO_2 adsorption was not carried out for wet shales because the experimental temperature is 0 °C which is hard to hold the moisture in the wet sample under low pressure. Besides, there is little or almost no difference between N_2 and CO_2 SA on dry samples, which suggesting N_2 can penetrate all ultra-micropores of wet samples [15]. The free space test by helium on the instrument was not used for the low-pressure gas sorption isotherms since an automatic warm free space test would expose the equilibrated moisture samples to a vacuum which would remove the moisture. Thus, the skeletal densities of wet and dry shales measured by Helium pycnometry were used to calculate the warm and cold free space manually to obtain the correct gas sorption results. The bulk density of dry shales was obtained from Mercury intrusion porosimetry by Micromeritics Autopore IV Series instrument at 0.035 bar [15].

2.5 High-pressure methane adsorption

High-Pressure Volumetric Analyzer (HPVA-100) was used to measure the high-pressure methane adsorption of shale by the static volumetric method. Approximately 10 g shale particles (2-4 mm) wet and dry were weighed and loaded into the 10 mL stainless steel sample cell and sealed before the measurement. Each sample was analyzed in triplicate to assess errors. For the dry measurement, all the samples in the cell were degassed at 120 °C for 48 hours first, and then the methane adsorption isotherms were acquired. A sample pre-evacuation was carried out for 45 minutes to reach a vacuum setpoint of 0.013 bar on the high-pressure instrument, and an isotherm was generated from 0 to 105 bar with a 45-minute equilibration time per pressure point. For the wet shales, all the methane adsorption isotherms were obtained from 1.2 to 105 bar at 25 °C, avoiding the wet samples being subjected to a vacuum on the high-pressure instrument. The mass deviation of wet shales before and after analysis was ±0.0018%. Similar free space corrections were carried out on this instrument as for the low-pressure gas sorption method using skeletal density and manually calculating warm and cold free spaces.

The actual adsorbed layer should be represented by the absolute amount, and this is the gas quantity that needs to be considered rather than the surface excess amount obtained by the volumetric sorption measurement. The Gibbs equation (equation (1)) [13, 50] is used in order to do the conversion, since the difference between excess and absolute amount adsorbed is non-negligible at higher pressure exceeding 10 bar [12]. The dual-site Langmuir model, which is suitable for heterogeneous adsorbents [13, 14] is used in this study to predict the methane adsorption at pressures over 105 bar. The equation for the dual-site Langmuir can be written in the following form (equation (2).

$$Q_a = Q_e + (V_a \times \rho_g) \quad (1)$$

$$Q_a(P,T) = Q_{max} \times \left[(1-\alpha)\frac{b_1(T)P}{1+b_1(T)P} + \alpha\frac{b_2(T)P}{1+b_2(T)P}\right] \quad (2)$$

Where, Q_a is the absolute adsorption quantity; Q_e is the excess adsorption quantity; Q_{max} is the max absolute adsorption quantity; V_a is the pore volume for gas to adsorb into; ρ_g is the density of the bulk gas; $b_1(T)$ and $b_2(T)$ are the temperature-dependent equilibrium constants, which are related to the energy of adsorption sites; $b_1(T)$ and $b_2(T)$ are weighted by a coefficient (α); α is the fraction of the second type of site ($0 < \alpha < 1$); P is the pressure; T is the temperature.

2.6 Gas Chromatography-Mass Spectrometry

Extracted oils from the shales were analyzed by gas chromatography-mass spectrometry (GC-MS) using Agilent GC-MS (7890B GC; 5977A-mass selective detector (MSD)) in splitless mode. Product separation was performed on an HP-5MS column (30 m × 250 µm × 0.25 µm). The GC oven temperature was initially held at 50 °C for 0.5 min, then heated to 300 °C at a rate of 4 °C/min, where it was held for 5 minutes. The MS (EI of 70 eV) was scanned in the mass range of m/z 40–400, with an ion source temperature of 200 °C. Individual compounds were identified using a NIST 14 MS library and published data.

3. Results and Discussion

3.1 Shale characterization and geochemistry

Basic information on the shales, including their formation, bury depth, TOC, maturity, moisture content of wet samples, and the yield of extracted organic matter, are listed in Table 1. The shales from different formations and depths have TOC contents ranging from 2.4 to 5.1 wt.%. Shales SH1 (2.95% Ro) and SH2 (2.58% Ro) are overmature, BS3 (1.01% Ro) is oil-window maturity and GH4 (1.95% Ro) is gas-window maturity. The moisture contents of the initial and extracted shales are in the ranges 1.22-2.72 and 1.13-2.06 wt.%, respectively, indicating the extracted shales adsorb less water with reductions of 15, 7, 37, and 25% for SH1, SH2, BS3, and GH4, respectively. The yield of extractable oil decreases with increasing maturity from 2.5 wt.% TOC for the oil-window shale, BS3 to 1.1 wt.% TOC for the gas-window shale, GH4, and 0.3-0.5 wt.% TOC for the over-mature shales,

SH1 and SH2. The extracted oil volumes range from 0.13 to 0.73 µL/g, assuming the extracted oil density is 0.85 g/m^3, which is the same as light crude oil [51, 52].

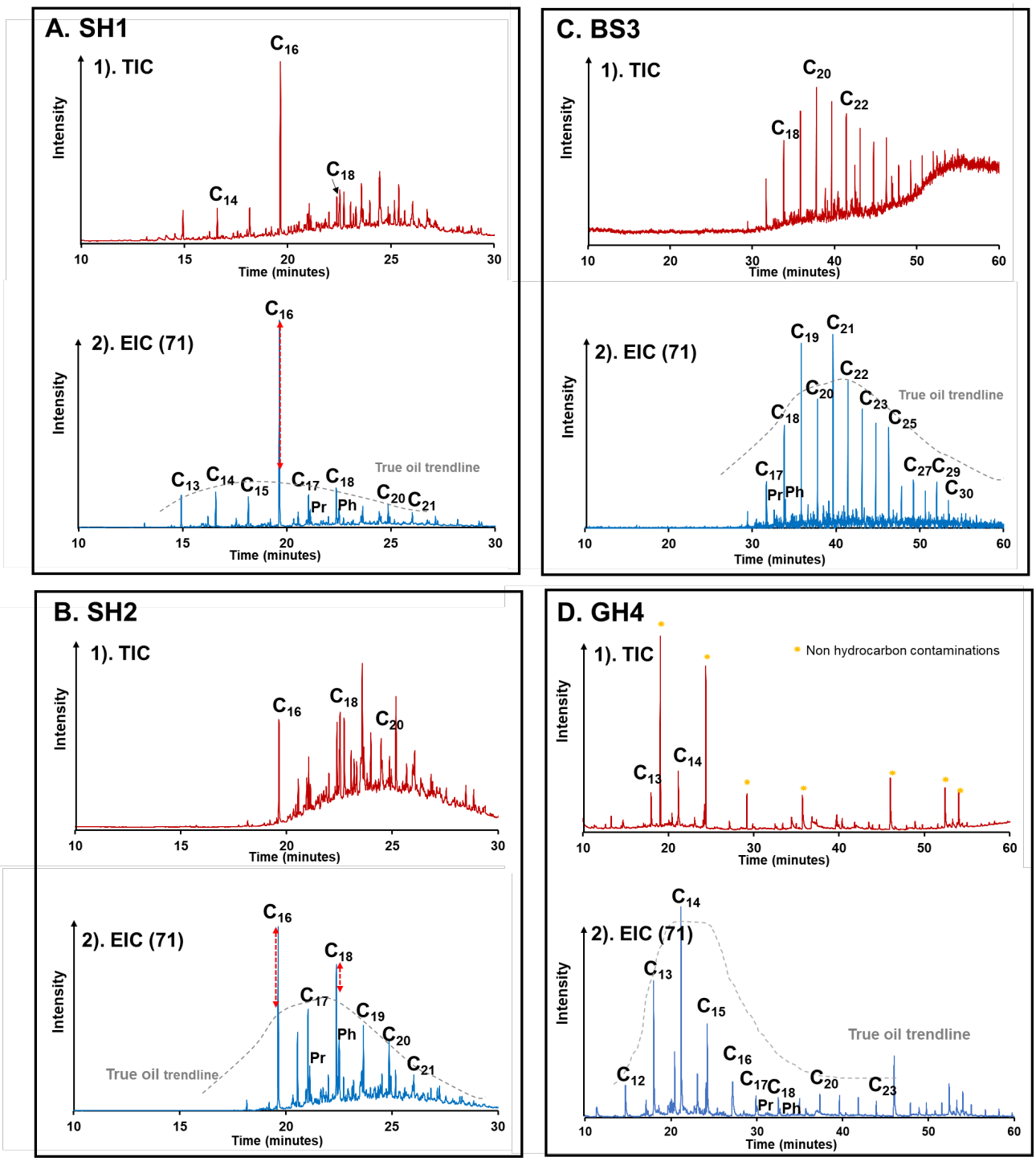
Table 1. Characteristics of the initial and extracted shales

Sample	Formation	Depth (m)	TOC (wt.%)	Maturity (% Ro)	Moisture (wt.%)	Oil Yield (wt.% TOC)	Oil volume (V_{oil}) (µL/g)
Initial SH1	Ordovician - Lower Silurian Wufeng-Longmaxi, China	4119	5.1	2.95	1.50[a]	0.3	0.17
Ext SH1					1.27[b]		
Initial SH2	Ordovician - Lower Silurian Wufeng-Longmaxi, China	4098	2.4	2.58	1.22[a]	0.5	0.13
Ext SH2					1.13[b]		
Initial BS3	Carboniferous Bowland Becconsall, UK	2143	2.5	1.01	1.84[a]	2.5	0.73
Ext BS3					1.17[b]		
Initial GH4	Carboniferous Bowland Grange Hill, UK	3113	3.4	1.95	2.72[a]	1.1	0.44
Ext GH4					2.06[b]		

The TOC, moisture, and oil yield were the average data from triplicate determinations. Moisture[a] is the moisture content for the initial shale, and moisture[b] is that for extracted shale.

3.2 GC-MS characterization of the extracted oils

Figure 1 shows the total ion chromatograms (TIC) and m/z 71 single ion chromatograms (EIC 71) for the oils extracted from the four shales with the *n*-alkane peaks labelled. The oil from the oil-window shale, BS3, is characteristic of a paraffinic oil with *n*-alkanes prominent ranging from C_{16} to C_{33} and the pristane to phytane ratio close to 1 (Figure 1C). Although the Bowland shale is a mixture of Type II/III and IV kerogens [53, 54], the oil has been generated predominately from the Type II kerogen present. The yield of oil extracted from the gas-window Bowland shale sample (GH4) was much lower than that for the oil-window shale (BS3) and is considerably lighter with n-alkanes from C_{12} to C_{23} (Figure 1D). Further, there is evidence of some non-hydrocarbon contamination from siloxane and methyl esters which are likely to rise from column bleed and the septa of the GC or the vial cap.



223 Figure 1. GC-MS total ion and m/z 71 single ion chromatograms for the extracted oil with the *n*-
224 alkane peaks labelled. A, B, C, and D are the oils from SH1, SH2, BS3, and GH4.

225 For the two over-mature shales where the extractable oil yields are low, light condensate would be

226 expected with possibly small quantities of residual oil. The extractable oils are relatively heavy and

227 contain *n*-alkanes in low concentrations. However, the fact that the *n*-alkanes do not extend beyond

228 n-C_{23} would suggest that they could arise from a small quantity of remaining oil. *n*-Hexadecane

dominant in the extract from SH1 (Figure 1A) is possibly drilling fluid-derived and, similarly, although much less pronounced the slightly elevated concentrations of *n*-hexadecane and *n*-octadecane over the other n-alkanes in the extract from SH2 (Figure 1B) [55]. The majority of the TICs for the extracts from the two over-mature shales comprise complex mixtures extending beyond C_{30}. The common drilling mud 'oil' bases including the diesel, enhanced-mineral oil (EMO), and synthetics (olefins and esters). The oil contaminated by the diesel and EMO shows a relatively higher peak of C_{16} in GC data [55]. The evidence would suggest that EMOs account for most of the complex mixtures extracted from SH1 and SH2.

3.3 Impact of solvent extraction impact on nanoporosity

The pore SA, micro, meso, macro, total nanopore volumes (pore size less than 100 nm), and their changes after solvent extraction calculated from the low-pressure N_2 and CO_2 gas isotherms are compared in Table 2. The different pore volume percentages for the dry and wet initial and extracted shales are presented in Figure 2. The SA and pore volumes of the dry shales decrease as the maturity decreases, in the order of SH1>SH2>GH4>BS3 (Table 2). This suggests that higher maturity shales generally develop more pores, which is consistent with previous studies [19, 56-59]. Although mesopores are dominant in the dry shales (Figure 2), the micropores still occupy a significant fraction of the pore volume. The contributions of micropores to the total nanopore volume are much higher in the over mature shales, SH1 and SH2, than those in the gas-window shale GH4 and oil-window shale BS3 (Figure 2), suggesting hydrocarbon generation facilitates the development of micropores [59-61].

Increases in pore volume are expected after any native oil is extracted [3, 28]. However, for the dry over mature shales, the changes (<20 %) in surface area and nanopore volume are small (Table 2) due to the low extraction yields (<0.5wt.% TOC, Table 1), with the extracted material being mainly drilling mud derived. Since the permeability of shales (typically less than 0.001 mD) is very low [62]

[63] [64], it is difficult for the drilling muds to penetrate the shale bulk, with most being on the surface. Solvent extraction may cause additional effects, such as contributing to the swelling of clay pores by the solvent [65] or changing the interactions with rocks if solvent adsorbing on clay surfaces or absorbing in kerogens [3, 28], which could interrupt the physical interactions between shales and adsorbed gas leading the measured SA and pore volume decreasing after extraction.

Table 2. Surface area and pore volumes of dry and wet shales.

Sample Name	BET SA(m^2/g)	V_{micro}(μL/g)	V_{meso}(μL/g)	V_{macro}(μL/g)	V_{nano}(μL/g)
Dry Initial SH1	21.73	6.9	11.7	0.75	19.3
Dry Ext SH1	19.11	5.7	11.8	0.87	18.4
SH1 Change*	**-12%**	**-17%**	**1%**	**15%**	**-5%**
Dry Initial SH2	16.70	5.37	6.7	0.16	12.2
Dry Ext SH2	16.67	5.42	6.5	0.14	12.1
SH2 Change*	**-0.2%**	**1%**	**-2%**	**-17%**	**-1%**
Dry Initial BS3	0.13	0.098	0.34	0.11	0.55
Dry Ext BS3	0.26	0.160	0.72	0.20	1.1
BS3 Change*	**92%**	**64%**	**110%**	**78%**	**95%**
BS3 Oil P*	**-**	**9%**	**52%**	**12%**	**73%**
Dry Initial GH4	2.19	0.60	1.7	0.17	2.4
Dry Ext GH4	2.62	0.70	5.3	0.7	6.7
GH4 Change*	**20%**	**17%**	**222%**	**273%**	**176%**
GH4 Oil p*	**-**	**23%**	**845%**	**109%**	**977%**
Wet Initial SH1	0.075	0.0039	0.28	0.063	0.34
Wet Ext SH1	0.059	0.0081	0.20	0.051	0.26
SH1 Change*	**-21%**	**105%**	**-28%**	**-19%**	**-25%**
Wet Initial SH2	0.029	0.0	0.21	0.056	0.27
Wet Ext SH2	0.036	0.0033	0.16	0.042	0.20
SH2 Change*	**25%**	**-**	**-26%**	**-25%**	**-25%**
Wet Initial BS3	0.060	0.0	0.18	0.038	0.22
Wet Ext BS3	0.108	0.0	0.32	0.07	0.40
BS3 Change*	**79%**	**-**	**80%**	**98%**	**83%**
Wet Initial GH4	0.011	0.0	0.07	0.023	0.09
Wet Ext GH4	0.045	0.0012	0.25	0.089	0.34
GH4 Change*	**310%**	**-**	**257%**	**295%**	**268%**

SA_{BET} are the surface areas calculated by BET theory; V_{micro}, V_{meso}, V_{macro}, and V_{nano} are the micropores (<2 nm), mesopore (2-50 nm), macropore (50-100 nm), and the total nanopore volume (<100 nm) calculated by the NLDFT model. Change* (in bold) is the change in pore properties resulting from solvent extraction compared with initial shales. Oil P* is the potential contribution of the increased pore volume to storing the extracted oil, which is calculated by $Oil\ P^* = 100\% \cdot (V_{Ext\ p} - V_{Ini\ p})/V_{oil}$, where $V_{Ext\ p}$ is the pore volume of shale after extraction, $V_{Ini\ p}$ is the pore volume of initial shale, and V_{oil} is the extracted oil volume (Table 1). Oil P* was only calculated for BS3 and GH4 since these are the only shales containing oil generated by maturation.

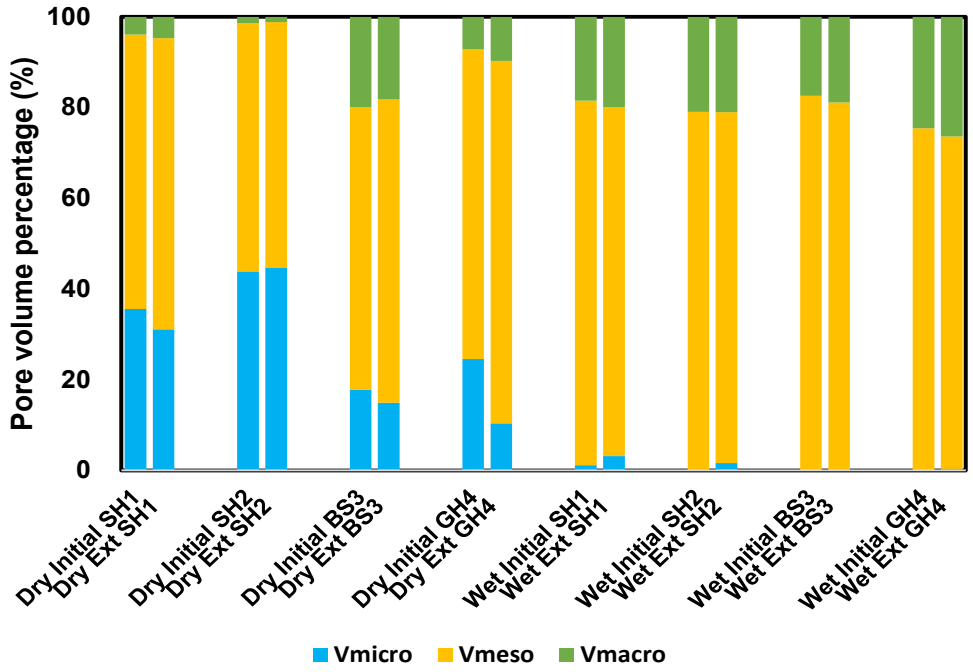


Figure 2. Micropore, mesopore, and macropore (<100 nm) volume percentages for the dry and wet initial and extracted shales.

The influence of solvent extraction is much larger for the two lower maturity shales. Table 2 indicates that the SA doubled from 0.13 to 0.26 m^2/g for dry BS3 and increased by 20% from 2.19 to 2.62 m^2/g for GH4. The total nanopore volume (up to 100 nm) also doubled for dry BS3 (from 0.55 to 1.1 µL/g) and increased by 176% for GH4 (from 2.4 to 6.7 µL/g). If the increased 64% micropore pore volume is generated solely by removing the oil, it is estimated that 9% of the extracted oil in shale BS3 is stored in the micropores (Oil p* in Table 2). The mesopores (from 0.34 to 0.72 µL/g) and macropores up to 100 nm (from 0.11 to 0.20 µL/g) increase by 110 and 78%, respectively, after oil extraction. This new porosity provides estimated storage space for 52 and 12%, respectively, of the extracted oil (64% in total). Similarly, for GH4, the increase of 17% micropore volume provides storage space for 23% oil, with the rest 77% oil stored in the mesopore or/and macropore, since the mesopores (from 1.7 to 5.3 µL/g) and 50-100 nm macropores volume (from 0.17 to 0.7 µL/g) increase by over 200% (Table 2). Clearly, for GH4, oil removal opens access to blocked

meso/macropores since the increase in pore volume is considerably greater than the volume of the extracted oil. For BS3, where the increase in pore volume accounts for 73% of the extracted oil, the implication is that some of the oil resides in macropores > 100 nm.

The aliphatic and aromatic hydrocarbons in oils are mainly stored in micro and mesopores, but the higher molecular mass polars and asphaltenes reside primarily in the macropores [3, 21, 28, 66]. The increase in macropore volume for the extracted shale is consistent with the non-hydrocarbons being removed by solvent extraction. The overall nanoporosity increases after extraction for the oil-window shale, BS3, and the gas-window shale, GH4 are larger than SH1 and SH2 since it is oil generated by maturation being extracted, as opposed to drilling fluids residing close to the surface.

As expected from our earlier studies [14, 15], most pore volume and SA are lost on wetting the shales (Table 2). Although mesopores are still dominant as for the dry shales, macropores replace micropores as the secondary pores in the wet shales (Figure 2), for both the initial and extracted samples. This arises from most of the micropores or micropore-necks being filled or/and blocked by water [15]. Solvent extraction provides a more complex influence on the pore system of wet shales. For extracted wet over-mature shales, SH1 and SH2, apart from micropore volume increasing (from 0.0039 to 0.0081 μL/g for wet SH1, and from 0 to 0.0033 μL/g for wet SH2), the mesopore, macropore and nanopore pore volumes all decrease slightly, with the reduction of -28, -19 and -25% for SH1, and -26, -25, -25% for SH2 (Table 2). The increase of micropores indicates there is less water to fill or block micropores in the extracted shales than initial shales as oil extraction did not enlarge micropores, mesopore, or macropores as discussed above. Larger micropores in extracted wet SH1 and SH2 could be due to the solvent interacting and altering the pore surface [3, 23, 28, 67], making it hard for water to condense or block micropores in solvent-extracted shales than initial shales. Additionally, the moisture contents of the extracted shales are also less than those of the initial

305 shales (Table 1), with reductions of 15, 7, 37, and 25% for wet SH1, SH2, BS3, and GH4, respectively,
306 suggesting less water is absorbed.

307 For the wet BS3 and GH4 shales, apart from the micropore volume of BS3 remaining close to zero,
308 all the other pore volumes display increases after solvent extraction (Table 2), For BS3, these are
309 80% for mesopores (from 0.18 to 0.32 μL/g), 98% for macropores (from 0.038 to 0.07 μL/g) and 83%
310 for the total nanopores (from 0.22 to 0.40 μL/g) volumes are increasing for wet BS3. Large
311 proportional increases are observed for GH4, the micropores increase from 0 to 0.0012 μL/g, being
312 257% for mesopores (from 0.07 to 0.25 μL/g), 295% for macropores (from 0.023 to 0.089 μL/g) and
313 268% total nanopores (from 0.09 to 0.34 μL/g). The increases in wet shales show a similar pattern
314 to dry samples. The pore volume increases for the wet extracted BS3 and GH4 shales are due to a
315 combination of oil removal enlarging the pores and the extracted shales having lower moisture
316 contents.

317 Overall, as well as water, the results indicate that extracted oil can have a significant impact on pore
318 characteristics. Although overmature shales have the largest pore volume, almost no oil remains, as
319 most of the oil has migrated. The limited pore system changes of overmature shales before and
320 after solvent extraction indicate solvent extraction would not destroy the shale original pore system,
321 only changing the interaction of shale pore surface. The oil generated by maturation mainly resides
322 in the pores less than 50 nm (micropores and mesopores) for the early to high mature shales, and
323 removing the oil increases the accessible pore volume no matter for dry or wet shales.

324 ### 3.4 Impact of solvent extraction impact on methane adsorption

325 The methane adsorption isotherms of the initial and solvent extracted shales are compared in
326 Figures 3 and 4, for the dry and moisture-equilibrated samples, respectively. The equilibrium
327 methane adsorption capacities (Qm) derived from the isotherms are listed in Table 3. For the initial

samples, the solubility of methane in oils has been estimated by Henry's Law, assuming that the methane is accessible to all the extractable oil. Thus, the estimated amount of adsorbed methane after Henry's law is the difference between the total amount of methane taken up by the samples and the dissolved methane estimated by Henry's Law linear plots in Figures 3 and 4. For the dry samples, the two over-mature shales, SH1 and SH2, have the higher equilibrium adsorption capacities, 77 and 127 mg/g TOC, respectively, compared to 16 and 21 mg/g TOC, respectively for the oil and gas window shales, BS3 and GH4, for the dry samples (Figure 3).

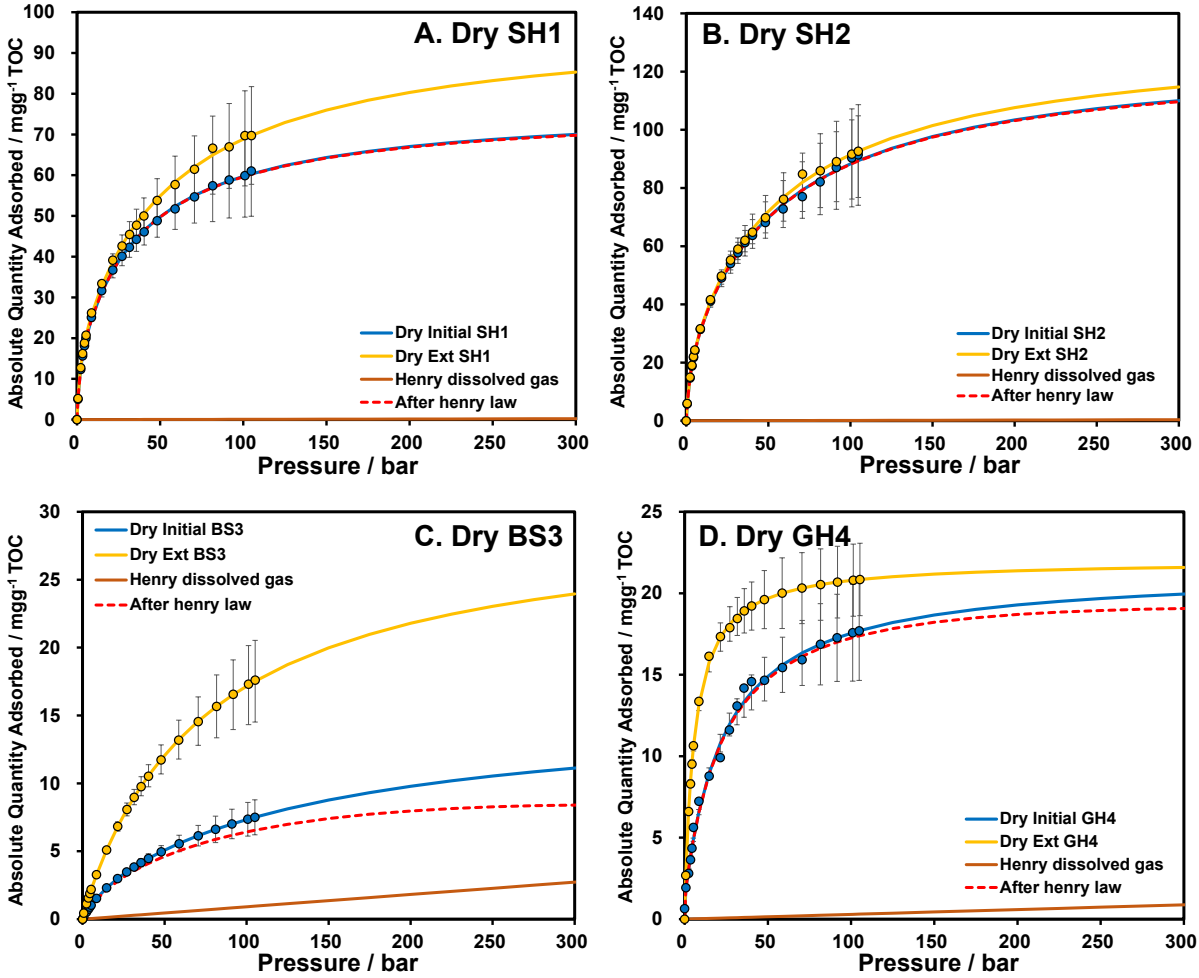


Figure 3. Methane adsorption isotherms of the dry initial shales, dry solvent extracted shales, after henry law correction for initial shales, and the dissolved methane uptakes calculated by Henry's Law.

Shales SH1, SH2, and BS3 have type I(b) isotherms, with shale GH4 having a type I(a) isotherm displaying a steeper isotherm at low pressures (Figure 3), arising mainly from narrow micropores (width <1 nm) [43]. For overmature dry shales, SH1 and SH2 (Figures 3A and B), although the average

methane adsorption isotherms of extracted shales are higher than the initial shales, with the Qm increased 27% (from 77 to 98 mg/g TOC) for SH1 and 5% (from 127 to 133 mg/g TOC) for SH2, they are still within the error range, suggesting the methane adsorption capacities of initial and extracted shales are relatively close. Thus, solvent extraction shows little impact on their methane adsorption capacities. Further, even deducting the potential contribution from dissolved methane in the low yields of extracted oil, the methane adsorption isotherms after the Henry's Law correction has very little impact, with the methane adsorption amount at 300 bar (Q_{300bar} is used as there is no Qm for henry law) changing by only *ca*. 0.3% for SH1 (from 70.0 to 69.8 mg/g TOC) and SH2 (from 110.0 to 109.6 mg/g TOC).

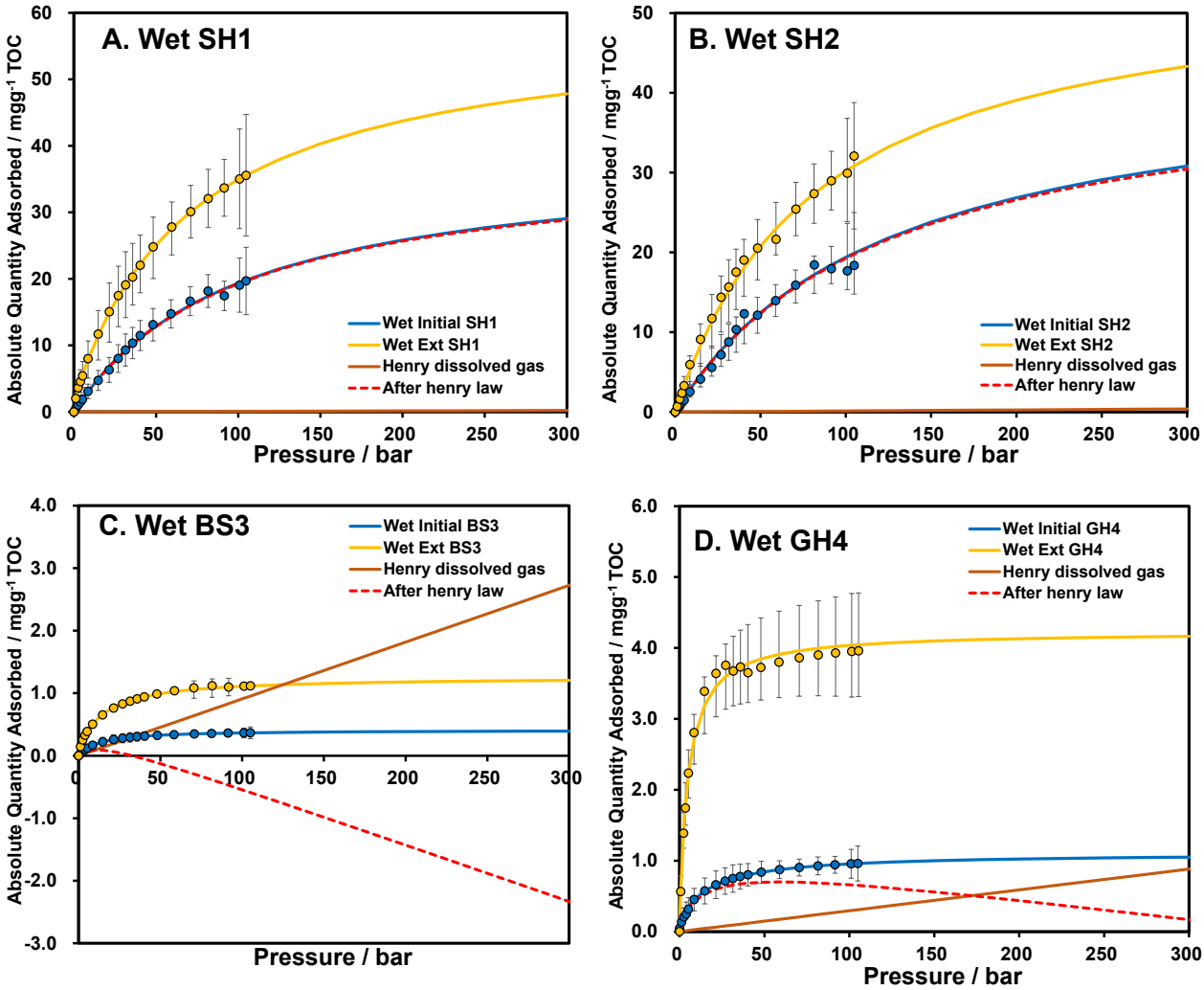


Figure 4. Methane adsorption isotherms of the wet initial and extracted shales, showing the Henry's Law corrections for dissolved methane in the oil present.

In contrast to the overmature shales, removing the residual oil increases the methane adsorption capacities of dry oil-window shale, BS3 significantly (Qm increased 90% from 16 to 30 mg/g TOC), A smaller increase is observed for dry gas-window shale GH4 (Qm increased 3% from 21 to 22 mg/g TOC) consistent with the lower yield of extractable oil compared to BS3. A steeper uptake at low pressure (<50 bar) of extracted GH4 isotherm is observed (Figure 3D), which indicates removing extracted GH4 oil increases narrow micropores (<1nm) [43], consistent with the oil being relatively light (section 3.2). Although isotherms are less steep after the Henry's Law correction for dry shales, the isotherm type remains the same, with their shapes being similar in the low-pressure range (<50 bar, Figure 3). The Henry's Law corrections reduce Q_{300bar} for BS3 (from 11.1 to 8.4 mg/g TOC) (Figure 3C) and GH4 (from 20.0 to 19.1 mg/g TOC) (Figure 3D) by 25 and 4.4%, respectively. However, this assumes that all the oil is accessible to the methane, if this is not the case, the impact of dissolved methane will be much less.

Table 3. The methane adsorption amount of dry, wet, initial, and extracted shales.

Adsorption (mg/g TOC)	Initial SH1	Ext SH1	*Qm Change SH1(%)*	Initial SH2	Ext SH2	*Qm Change SH2 (%)*	Initial BS3	Ext BS3	*Qm Change BS3 (%)*	Initial GH4	Ext GH4	*Qm Change GH4 (%)*
Dry Q_{300bar}	70.0	85.3	-	110.0	114.7	-	11.1	24.0	-	20.0	21.6	-
Dry Qm	77	98	***27***	127	133	***5***	16	30	***90***	21	22	***3***
Wet Q_{300bar}	29.1	47.8	**-**	30.8	43.3	**-**	0.4	1.2	**-**	1.1	4.2	**-**
Wet Qm	39	59	***52***	44	55	***27***	0.4	1.3	***207***	1.1	4.2	***282***
Qm Reduction (%)	**50**	**40**	**-**	**66**	**58**	**-**	**97**	**96**	**-**	**95**	**81**	**-**

Qm is the equilibrium methane adsorption capacities; Q_{300bar} is the methane adsorption amount at 300 bar; Q change (%) is the methane adsorption amount changes before and after the extraction; Qm Reduction (%) is the methane adsorption reduction for wet samples compared with corresponding shales.

Methane adsorption capacities of both the initial and extracted shales are reduced after moisture equilibration due to micropores being blocked (Table 3) [15]. The reductions in Qm for the initial shales, SH1, SH2, BS3, and GH4 are 50, 66, 97, and 95%, respectively, which are larger than the extracted samples (40, 58, 96, and 81%, respectively), suggesting moisture has a slightly reduced impact for the extracted shales since they adsorbed less water (Table 1). Additionally, the methane adsorption capacities for the wet extracted shales are larger than for the initial shales (Table 3),

even considering the experimental errors (Figure 4). The Qm of wet extracted SH1 increased from 39 to 59 mg/g TOC), SH2 from 44 to 55mg/g TOC, BS3 (from 0.4 to 1.3 mg/g TOC), and GH4 from 1.1 to 4.2 mg/g TOC), representing increases of 52, 27, 207 and 282% compared to the wet initial shales (Table 3), consistent with the increase of accessible micropore volume for the extracted shales (section 3.3).

For wet overmature shales, SH1 and SH2, the Henry's Law corrections for dissolved gas had virtually no effect on the methane sorption capacities (Figure 4A and 4B). In contrast, the methane adsorption isotherms after Henry's Law show negative isotherms for BS3 and GH4 (Figure 4C, and 4D). This indicates that virtually none of the methane is accessible to the oil. This arises from water blocking the micropores or micropore necks. For both BS3 and GH4, solvent extraction significantly increases the methane adsorption capacities, by a factor of 3-4, compared to the initial moisture equilibrated shales by reducing the extent to which the pores are blocked by water.

4. GIP estimation

Understanding both the impact of extracted oil and moisture on porosity and gas adsorption properties is vital for an accurate evaluation of shale gas resources and the design of effective production strategies. Like moisture, the removal of oil generated by maturation can lead to an overestimation of GIP [15]. Equation (3) has been used to calculate GIP in this study. The porosities of the dry and wet shale used for calculating the free gas calculation are based on equations (4) and (5). Considering the buried depths of the four samples, the reservoir pressure and temperature for the overmature shales, SH1 and SH2, are estimated as 600 bar and 100 °C [15, 68] (Li et al., 2018; Tang et al., 2016), for the UK Bowland shales, BS3, 300 bar and 60 °C and GH4, 450 bar and 80 °C. The excess adsorbed gas content reduces about 45, 35, and 25 % at 100, 80, and 60 °C when compared with 25 °C [12, 69, 70].

$$GIP = Q_{free} + Q_a = Q_{free} + Q_e + V_a \times \rho_g = V_{tot} \times \rho_g + Q_e \quad (3)$$

$$Porosity_{dry} = \frac{V_{dry\ pore}}{V_{sh}} = 1 - \frac{\rho_{dry\ bulk}}{\rho_{dry\ sk}} \quad (4)$$

$$Porosity_{wet} = \frac{V_{wet\ pore}}{V_{sh}} = 1 - \frac{\rho_{wet\ bulk}}{\rho_{wet\ sk}} = 1 - \frac{\rho_{dry\ bulk}}{\rho_{wet\ sk}} \times (1 + W) \quad (5)$$

Where, Q_{free} is the free gas; Q_a is the absolute adsorption gas; Q_e is the excess adsorption gas; V_a is the pore volume for gas to adsorb into; ρ_g is the density of the bulk gas, which can be obtained from the REFPROP version 8.0 software; V_{tot} is the total pore volume accessible to gas in shale; $Porosity_{dry}$ is the total porosity of dry shale; $V_{dry\ pore}$ is the pore volume of dry shale; $Porosity_{wet}$ is the total porosity of wet shale; $V_{wet\ pore}$ is the pore volume of wet shale; V_{sh} is the shale sample volume; $\rho_{wet\ bulk}$ is the bulk density of wet shale, $\rho_{dry\ bulk}$ is the bulk density of dry shales from mercury intrusion porosimetry (MIP) at 0.035 bar, $\rho_{dry\ sk}$ and $\rho_{wet\ sk}$ are the skeletal densities of the dry and wet samples obtained from helium pycnometry; W is the moisture content.

The total porosity and GIPs estimated for the initial and extracted shales are compared in Table 4. Oil extraction increased the total porosity from 18.3 to 21.0% for the dry shales, BS3, and increases from 16.8 to 20.9% for the moisture equilibrated shale, which are much larger increases than the other shales, as BS3 has the highest oil yield (Table 4). Table 4 indicates that the estimated GIP increases with total porosity, in the order of GH4>BS3>SH1>SH2 for the initial shales under both dry and moisture equilibrated conditions. Although SH1 and SH2 have much larger adsorbed gas (Q_a) contributions, the free gas (Q_{free}) contributions controlled by the total pore volume are smaller than for BS3 and GH4 (Table 3). However, in all cases, the free gas contributions dominate the GIP estimates for the initial dry shales (82, 65, 99, and 98% for SH1, SH2, BS3, and GH4, respectively, Table 4). As expected, the GIP estimated for the moisture equilibrated shales are lower than for dry shales, with reductions of 32, 38, 11, and 12% observed for initial SH1, SH2, BS3, and GH4, respectively, with the reductions for the extracted moisture equilibrated shales being 27, 28, 4 and 14%, respectively, when compared with the corresponding extracted dry shales (Table 4). This confirms the GIP based on dry shales is significantly overestimated, as previous research indicated [15, 71, 72]. Moreover, moisture reduces the adsorbed gas (41-96%) more than the free gas (2-27%)

for both the initial and extracted shale (Table 4) since the impact of moisture is mainly blocking micropores for adsorbed gas rather than the larger pores accommodating most of the free gas.

Table 4. The porosity, total pore volume, and the estimated GIP of the initial and extracted shales.

Sample Name	Porosity (%)	V_{total} (m^3/t)	N_a (kg/t)	N_{free} (kg/t)	GIP (kg/t)	GIP change after extraction (%)
Dry Initial SH1	10.2	0.0432	2.1	9.3	11.4	6
Dry Ext SH1	10.2	0.0434	2.6	9.5	12.1	
Dry Initial SH2	4.0	0.0156	1.6	2.9	4.5	-3
Dry Ext SH2	3.8	0.0148	1.7	2.7	4.4	
Dry Initial BS3	18.3	0.0857	0.21	15.5	15.7	16
Dry Ext BS3	21.0	0.1008	0.44	18.2	18.7	
Dry Initial GH4	22.2	0.1046	0.44	22.8	23.2	3
Dry Ext GH4	22.8	0.1080	0.47	23.5	23.9	
Wet Initial SH1	6.8	0.0284	0.94	6.8	7.8	12
Wet Ext SH1	7.2	0.0304	1.5	7.3	8.8	
Wet Initial SH2	2.5	0.0095	0.49	2.3	2.8	11
Wet Ext SH2	2.7	0.0102	0.65	2.5	3.1	
Wet Initial BS3	16.8	0.0772	0.007	14.0	14.0	22
Wet Ext BS3	20.9	0.0990	0.022	17.9	18.0	
Wet Initial GH4	20.3	0.0930	0.023	20.3	20.3	1
Wet Ext GH4	20.2	0.0938	0.090	20.5	20.6	

V_{total} is the total pore volume calculated from the porosity of corresponding shales.

Overall, the changes arising from oil extraction are relatively small for the two overmature shales, SH1, SH2, and the gas window shale, GH4 (-3 to 6% for the dry shales and 1-12% for the moisture equilibrated shales, Table 4) with the largest changes being for the oil window shale, BS3. In contrast, Table 4 indicates that the GIP is overestimated by 16 and 22% for both dry and moisture equilibrated extracted oil window shale, BS3.

Clearly, the impact of solvent extraction on the estimated GIP is minimal for the two overmature shales investigated, especially compared to moisture (Table 4). In contrast, although some researchers believe removing oil in low maturity shale has little influence on methane adsorption [21], the impact of oil removal is significant for oil-window shales, with the GIP being over-estimated by 22% for the shale investigated here. For such shales, a combination of moisture equilibration and not extracting oil present generated by maturation is essential to obtain reliable GIP estimates.

5. Conclusions

1). Solvent extraction has limited impacts on the methane adsorption and pore texture for the dry overmature shales, SH1 and SH2, with the small amounts of extractable oil arising from drilling mud contamination. However, micropore volume and the methane adsorption capacities for the wet over mature shales increased after solvent extraction, possibly due to the reductions in moisture content, meaning there is reduced pore blocking.

2). More than 60% of the extractable oil resides in micro and mesopores for the oil-window BS3. Removing the oil increased the nano micro, meso, and macropore volumes by up to nearly 300% for the dry BS3 and GH4. The increases in methane adsorption capacities are proportionally greater for the wet shales (207-282%) compared to the dry shales (90 and 3%).

3). Henry's Law estimations have indicated that the proportions of dissolved gas in the dry shale samples is extremely small. For wet shales, not all the residual oil is accessible if water blocks some of the micropores, which means the dissolved gas calculated by Henry's Law could be significantly overestimated.

4). Solvent extraction increases the estimated GIP by 16% for the dry oil-window shale, BS3, and moisture reduces the GIP of the initial BS3 shale by 11%. The GIP for extracted wet shale is overestimated by 22%. The impact on GIP estimates was considerably less for the over-mature shales due to their low extractable oil contents. Nevertheless, this study indicates the significant impact that natural oil arising from maturation can have on the estimated GIP for oil-window shales.

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